

Carbonaceous Aerosol Processing in the Mexico City Metropolitan Area

Timothy B. Onasch¹, Jay G. Slowik², Paul Davidovits², Scott C. Herndon¹, Ezra Wood¹, Douglas R. Worsnop¹, Charles E. Kolb¹, W. Berk Knighton³, Miguel Zavala⁴, Dwight Thornhill⁵, Linsey Marr⁵, W. Patrick Arnott⁶, Claudio Mazzoleni⁷, Manvendra K. Dubey⁷, Rebecca J. Hopkins⁸, Mary K. Gilles⁸, Yury Desyaterik⁹, Alexander Laskin⁹

1. Aerodyne Research, Inc.; 2. Boston College; 3. Montana State University; 4. Massachusetts Institute of Technology; 5. Virginia Polytechnic Institute and State University; 6. Desert Research Institute of the Nevada System of Higher Education; 7. Los Alamos National Laboratory; 8. Lawrence Berkeley National Laboratory; 9. Pacific Northwest National Laboratory

Overview

As part of the Mexico City Metropolitan Area (MCMA) component of the MILAGRO campaign (March 2006), polydisperse and mobility-selected particles were sampled by a time-of-flight Aerodyne aerosol mass spectrometer (ToF-AMS) and a scanning mobility particle sizer (SMPS). Sampling was performed from the Aerodyne mobile laboratory, which contained an array of particle, gas-phase, and meteorological instrumentation. Simultaneous measurements by the AMS and SMPS instruments yielded the particle mass, volume, density, composition, dynamic shape factor, and fractal dimension.

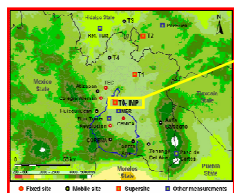
Two types of ambient particles were observed:

- (1) Fractal particles containing a refractory component assumed to be black carbon.
- (2) Near-spherical particles characteristic of regional-scale transport.

During the early morning, the ambient fractal particles were similar in morphology and composition to diesel-generated particles. However, as the morning progressed, the ambient fractal particles became larger and nearly spherical due to gas-to-particle condensation. The coatings on the fractal particles contained organic and inorganic compounds and are shown to be likely products of atmospheric photochemistry. The rate of photochemistry increased throughout the morning, as evidenced by ozone and particulate nitrate formation due to the increase in incident solar radiation.

The fractal particles were no longer evident after late morning due to morphological changes implying that primary soot emissions in a polluted urban environment are processed rapidly via photochemically driven gas-to-particle condensation. Further analysis will include the results from the other particle and gas-phase instruments making simultaneous measurements.

Sampling Location and Platform



Sampling was performed in Mexico City at the Instituto Mexicano Petrolero (ITO) supersite, see above, from March 27-30, 2006. The Aerodyne mobile laboratory was used to obtain correlated particle, gas-phase, and meteorological measurements (see right).

Measurements were performed on polydisperse and mobility-selected particles. Tandem measurements of an Aerodyne aerosol mass spectrometer and a scanning mobility particle sizer on the size-selected particles were used to obtain detailed information about the particle composition and morphology. This study is the first application of this AMS-SMPS technique^{2,3} to ambient particles.

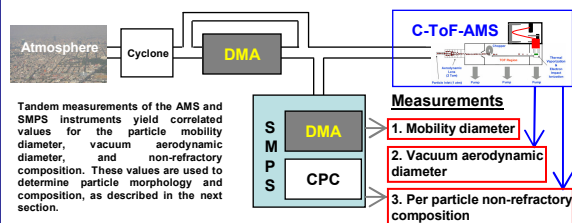
Sampling Platform: Aerodyne Mobile Laboratory



Comprehensive gas and particle instrument suite

- Multi-Angle Absorption Photometer (MAAP)
- Photoacoustic Spectrometer
- PAH Concentration (PAS2000)
- Filter Sampling for electron microscopy and chemical analysis
- Meteorological measurements
- Gas-phase measurements (CO₂, CO, NO₂, HNO₃, NH₃, O₃, NO, NO₂, NO_x, VOCs)

AMS-SMPS System for Particle Analysis



Tandem measurements of the AMS and SMPS instruments yield correlated values for the particle mobility diameter, vacuum aerodynamic diameter, and non-refractory composition. These values are used to determine particle morphology and composition, as described in the next section.

AMS-SMPS Particle Analysis: Theory

Volume Equivalent Diameter (d_{ve}) Dynamic Shape Factor (χ)

$$\text{Particle Volume} = \frac{\pi}{6} d_{ve}^3$$
$$\chi = \frac{\text{Drag on Particle}}{\text{Drag on Sphere of Equal Volume}}$$
$$d_{ve} = f(d_{ve}, \chi)$$
$$d_{ve} = f(d_{ve}, \chi, \rho_p)$$
$$m_p = \Sigma(m_{BC}, m_{non-refractory}) = f(d_{ve}, \rho_p)$$
$$d_{ve}, \chi, \rho_p, m_{BC}$$

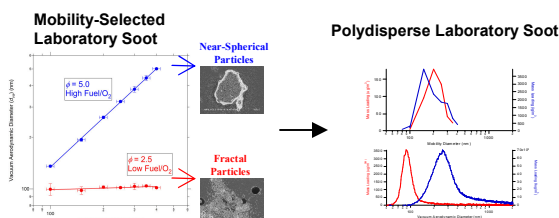
3 Equations, 4 Unknowns → underdetermined system

Solution: Express ρ_p in terms of mass and density of individual components.

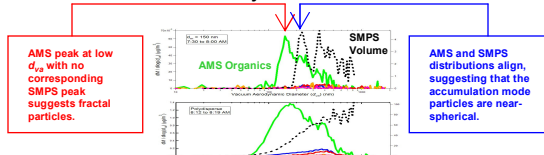
$$\rho_p = f(m_{BC}, m_{non-refractory}, \rho_{BC}, \rho_{non-refractory})$$

3 Equations, 3 Unknowns → system can be solved

Identification of Fractal and Near-Spherical Particles

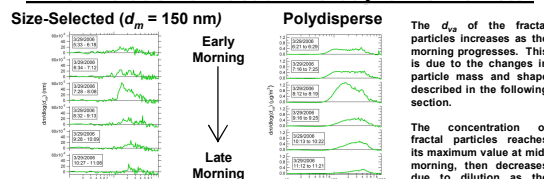


Mexico City: Ambient Particles

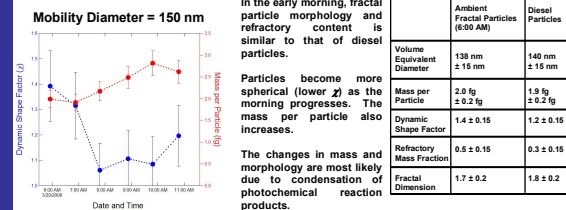


SMPS distributions are converted from mobility diameter to vacuum aerodynamic diameter assuming $d_{ve}/d_m = 1.3$, estimated from the mass spectrum. Fractal dimension (D_f) is determined using the mass-mobility relationship ($m_p \propto d_{ve}^{D_f}$) to be $D_f = 1.7$ for the ambient fractal particles and $D_f = 3.0$ for the accumulation mode particles.

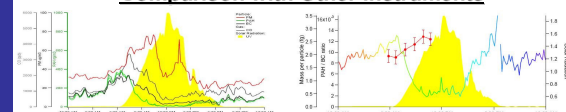
Time Evolution of Vacuum Aerodynamic Diameter



Time Evolution of Particle Mass and Shape

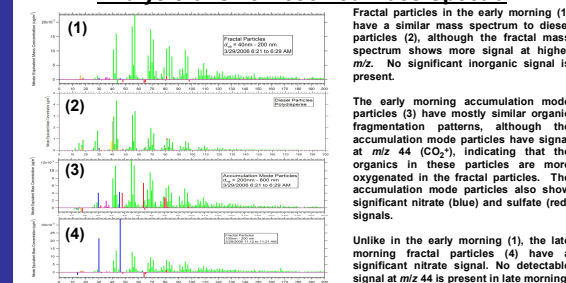


Comparison with Other Instruments



Black carbon (BC) measured by a MAAP and surface-bound PAH measured by a PAS2000 increase during morning rush hour. Both species decrease in late morning as the boundary layer rises due to increased solar radiation, however PAH decreases before BC.

Analysis of Size-Resolved Mass Spectra



Conclusions

- AMS-SMPS measurement technique can be used to distinguish ambient fractal and non-fractal particles. The C-ToF-AMS is sufficiently sensitive to enable determination of particle morphology and composition behind a DMA.
- As the morning progresses, fractal particles become more spherical and their mass per particle increases.
- Changes in the fractal particle mass and shape is likely due to increased condensation of photochemical reaction products.

Acknowledgements

Funding: Department of Energy, National Air and Space Administration, National Science Foundation

References

1. Kolb, C.E., Herndon, S.C., McManus, J.B., Shorter, J.H., Zahniser, M.S., Nelson, D.D., Jayne, J.T., Canagaratna, M.R., Worsnop, D.R. *Environ. Sci. Technol.* 38:5694-5703, 2004.
2. Slowik, J.G., Stankin, K., Davidovits, P., Williams, L.R., Jayne, J.T., Kolb, C.E., Worsnop, D.R., Rudich, Y., DeCarlo, P.F., Jimenez, J.L. *Aerosol Sci. Technol.* 38:1206-1222, 2004.
3. DeCarlo, P.F., Slowik, J.G., Worsnop, D.R., Davidovits, P., Jimenez, J.L. *Aerosol Sci. Technol.* 38:1185-1205, 2004.